Development of new xanthendiol derivative applied to the negative-tone molecular resist for EB/EUVL

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Motivation for Negative - Tone Resist

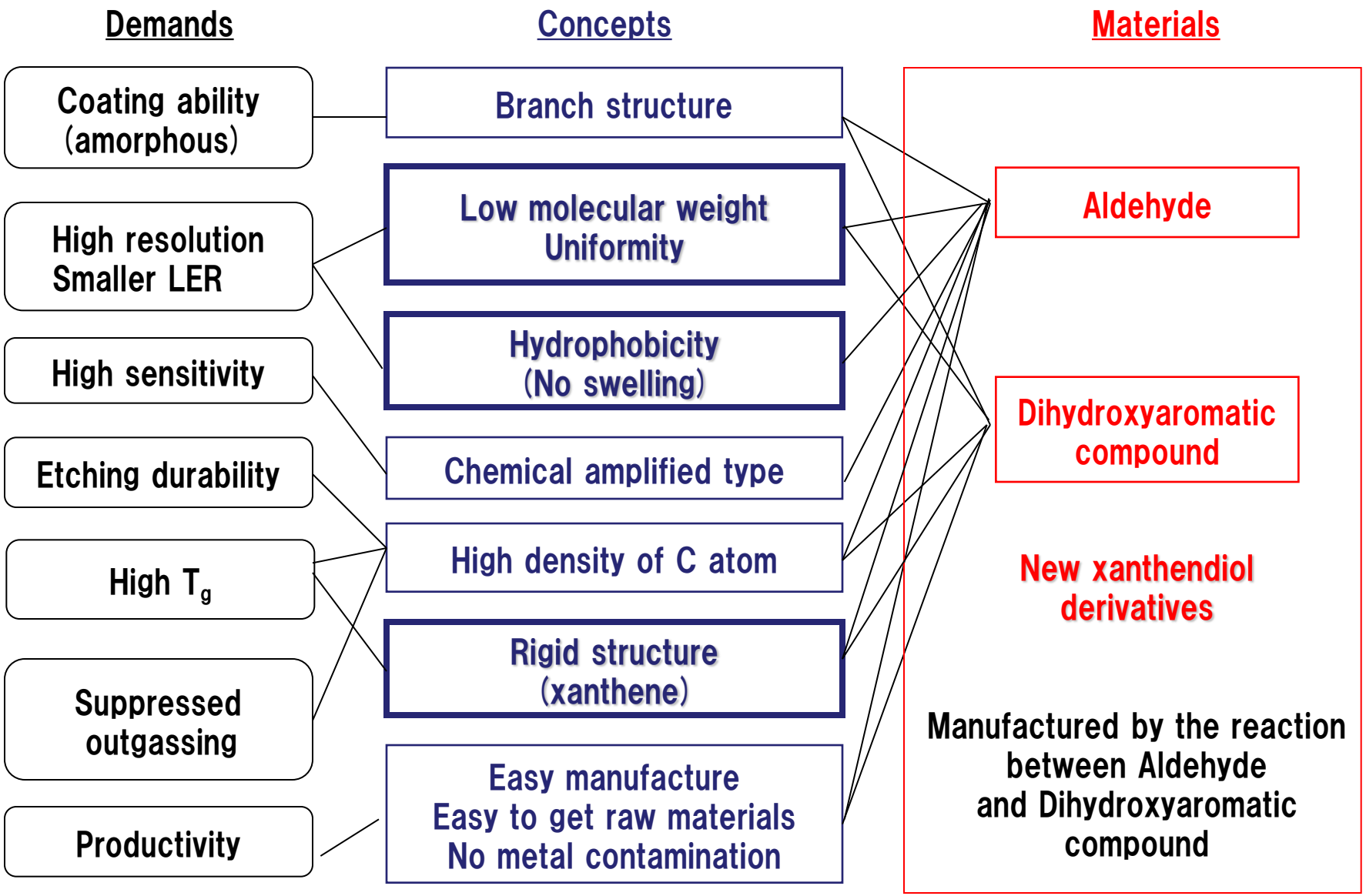
2012 ITRS Roadmap

Table LITH3A Resist Requirements

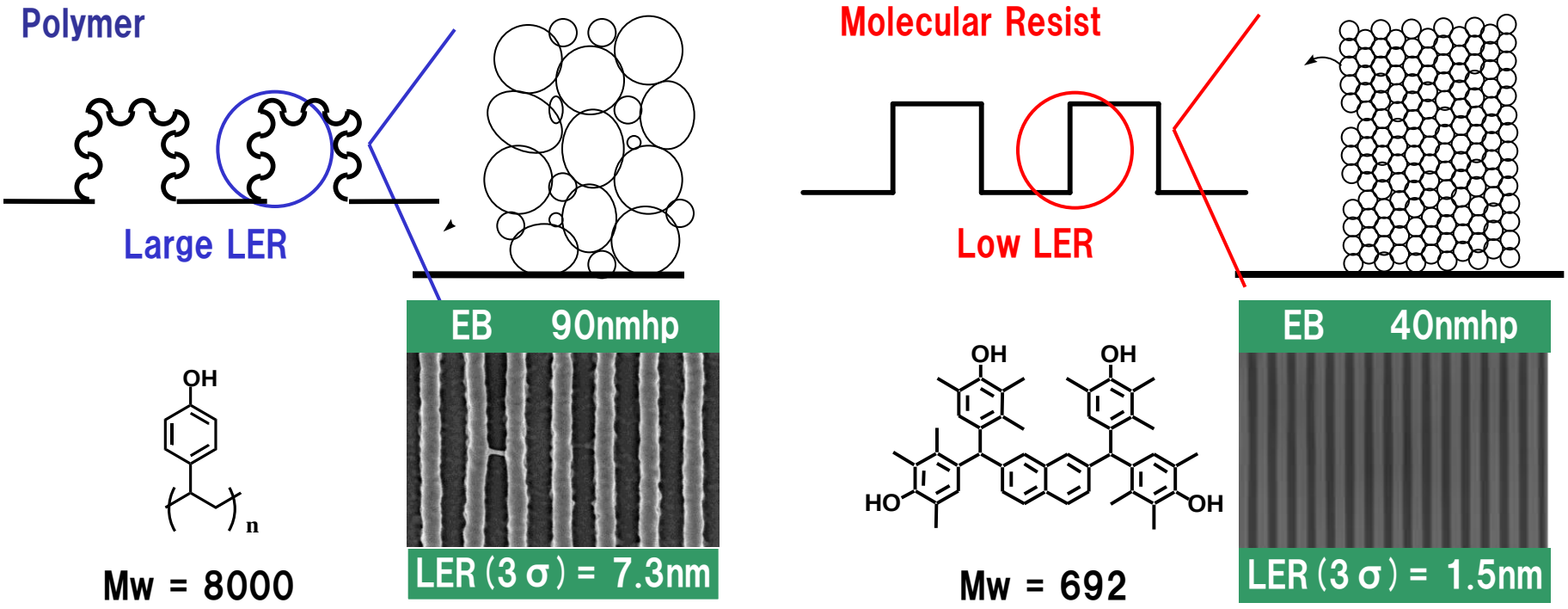
Year of Production	2011	2012	2013	2014	2015	2016	2017	2018	2019
DRAM ½ pitch (nm) (contacted)	36	32	28	25	23	20	18	16	14
Flash ½ pitch (nm) (un-contacted poly)	22	20	18	17	15	14	13	12	11
MPU/ASIC Metal 1 (M1) ½ Pitch (nm)(contacted)	38	32	27	24	21	19	17	15	13
MPU gate in resist length (nm)		22 31	**28**	18 25	17 22	**20**	14 18	13 16	**14**
Resist meets requirements for gate resolution and gate CD control (nm, 3 sigma) **†	2.3	2.1	1.9	1.8	1.7	1.6	1.5	1.3	1.2
Resist thickness (nm, single layer) ***	40-80	40-75	35-65	30-60	30-55	25-50	25-50	20-45	20-40
PEB temperature sensitivity (nm/C)	1	1	0.8	0.8	0.8	0.8	0.6	0.6	0.6
Backside particle density (particles/cm^2)	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
Back surface particle diameter: lithography and measurement tools (nm)	100	100	75	75	75	50	50	50	50
Defects in spin-coated resist films (#/cm^2) †	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Minimum defect size in spin-coated resist films (nm)	20	20	20	20	10	10	10	10	10
Defects in patterned resist films, gates, contacts, etc. (#/cm^2)	0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.01
LWR (3sigma) <8% of CD	2.8	2.5	**2.2**	2.0	1.8	**1.6**	1.4	1.3	**1.1**
Defects in spin-coated resist films for double patterning (#/cm2)	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Backside particle density for double patterning (#/cm2)	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14	0.14

Negative-tone resists are limitedly influenced by flare.
We believe Negative-tone resist can achieve these required properties.

Design Concepts for New Negative-tone Molecular Resist Material



Motivation for negative-tone molecular resist

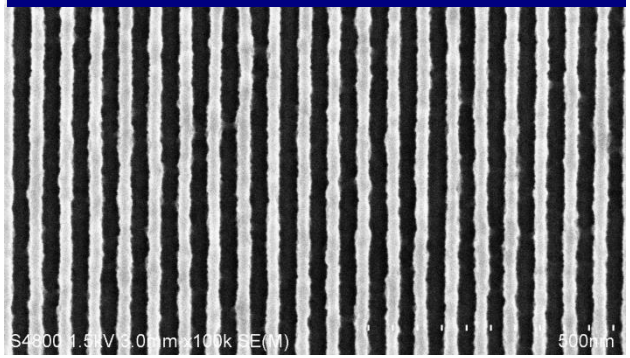


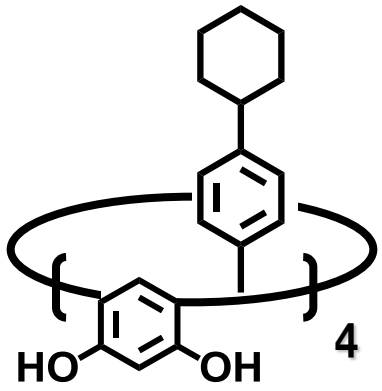
– Phenylcalix [4] resorcinarenes are small-size and high-Tg molecules, enough for patterning high-resolution and low-LER.

Our proposal for molecular resist materials.
M. Echigo et al., *5th International EUV Symposium*, **01-RE-27** (2006)

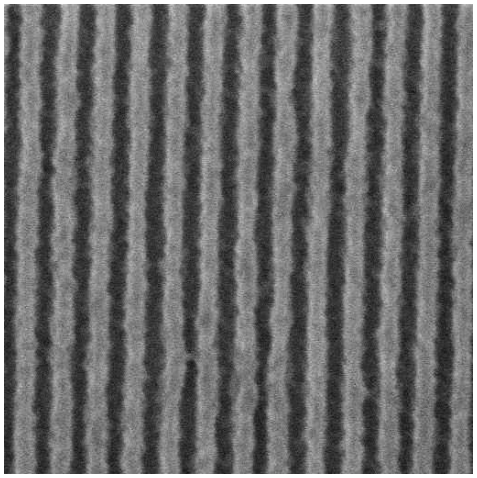
Previous Data (Negative-tone resist using MGR108)

EB 30nm hp,60nmt
52 μC/cm²





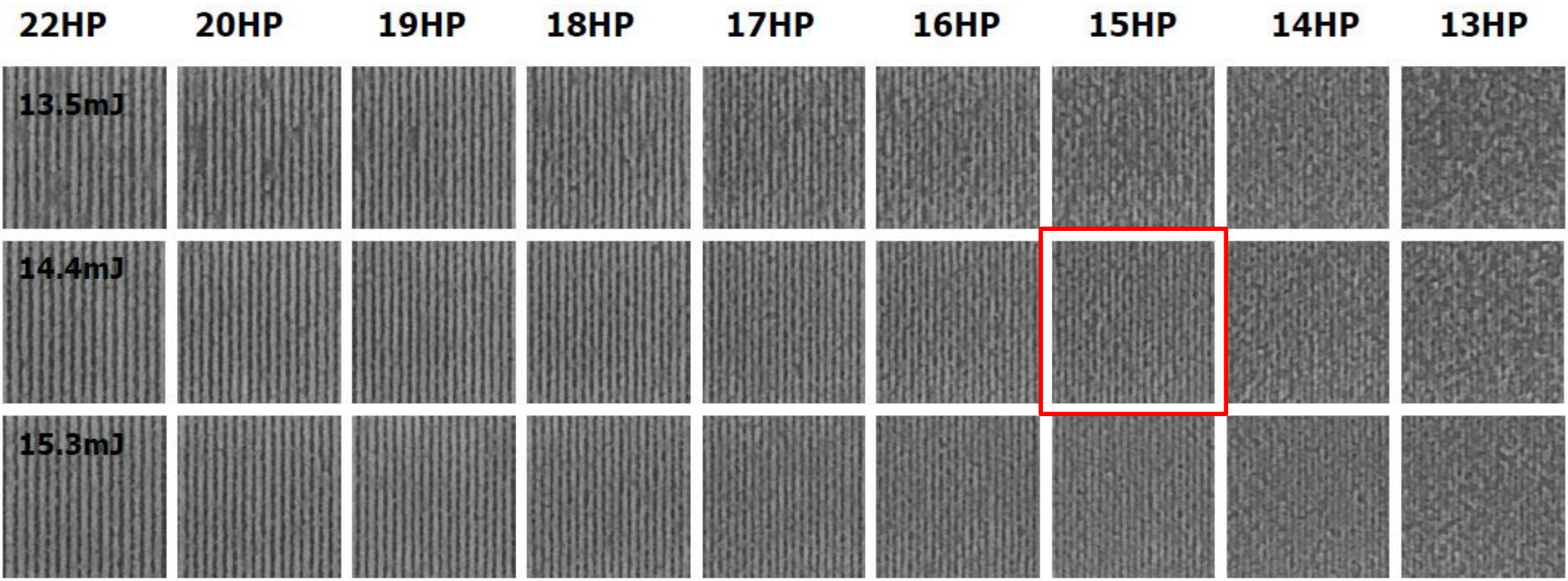
MGR108

EUV LS Pattern	
CD (nm)	26
Esize (mJ/cm²)	24.0
LWR (nm)	6.1
nZ (32)	12.8

By courtesy of SEMATECH

- Patterns were well defined at ≦30 nmhp.

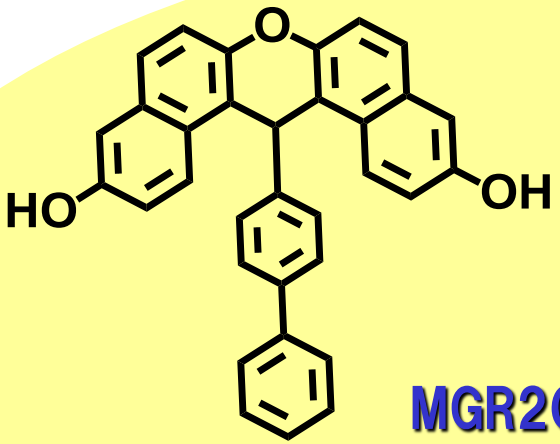
Applied example (Negative-tone resist using MGR108)



Substrate : Si with HMDS
Film thickness : 60nm
Apparatus : LBNL-MET(0.3NA,Pseudo-PSM F2X)
Developing solution: TMAH

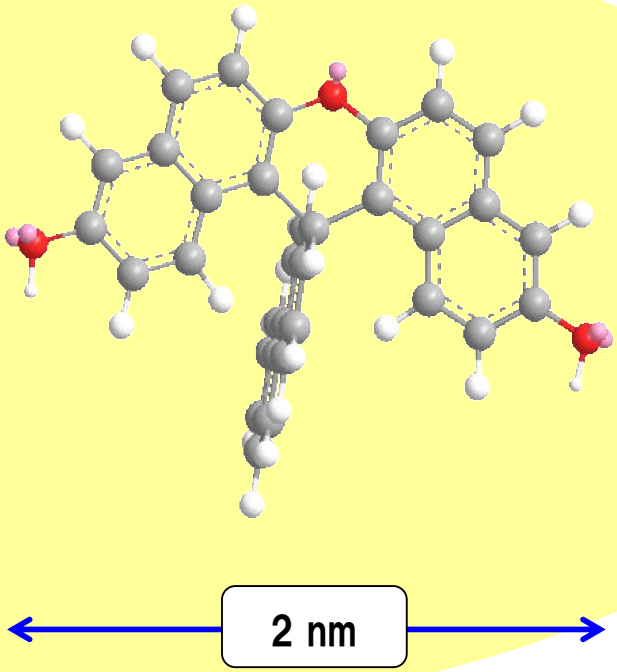
- Applied resist containing MGR108 patterned 15nm dense L/S at 14mJ/cm² with LBNL-MET.

Development of xanthendiol derivative



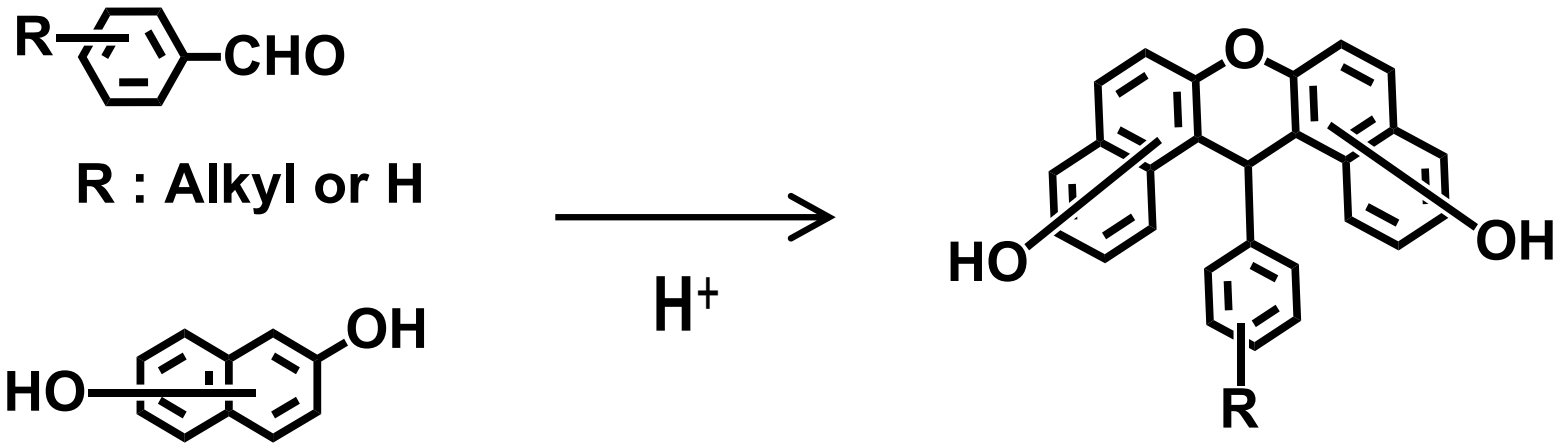
MGR202

Chemical Formula: $C_{33}H_{22}O_3$
Molecular Weight: 466.53
Elemental Analysis:
C, 84.96; H, 4.75; O, 10.29



- 13-Biphenyl-13H-benzoxanthen-3,10-diol, MGR202, was developed.

General synthesis of xanthendiol derivative



Xanthendiol derivatives were synthesized between aldehyde and dihydroxynaphtalene.

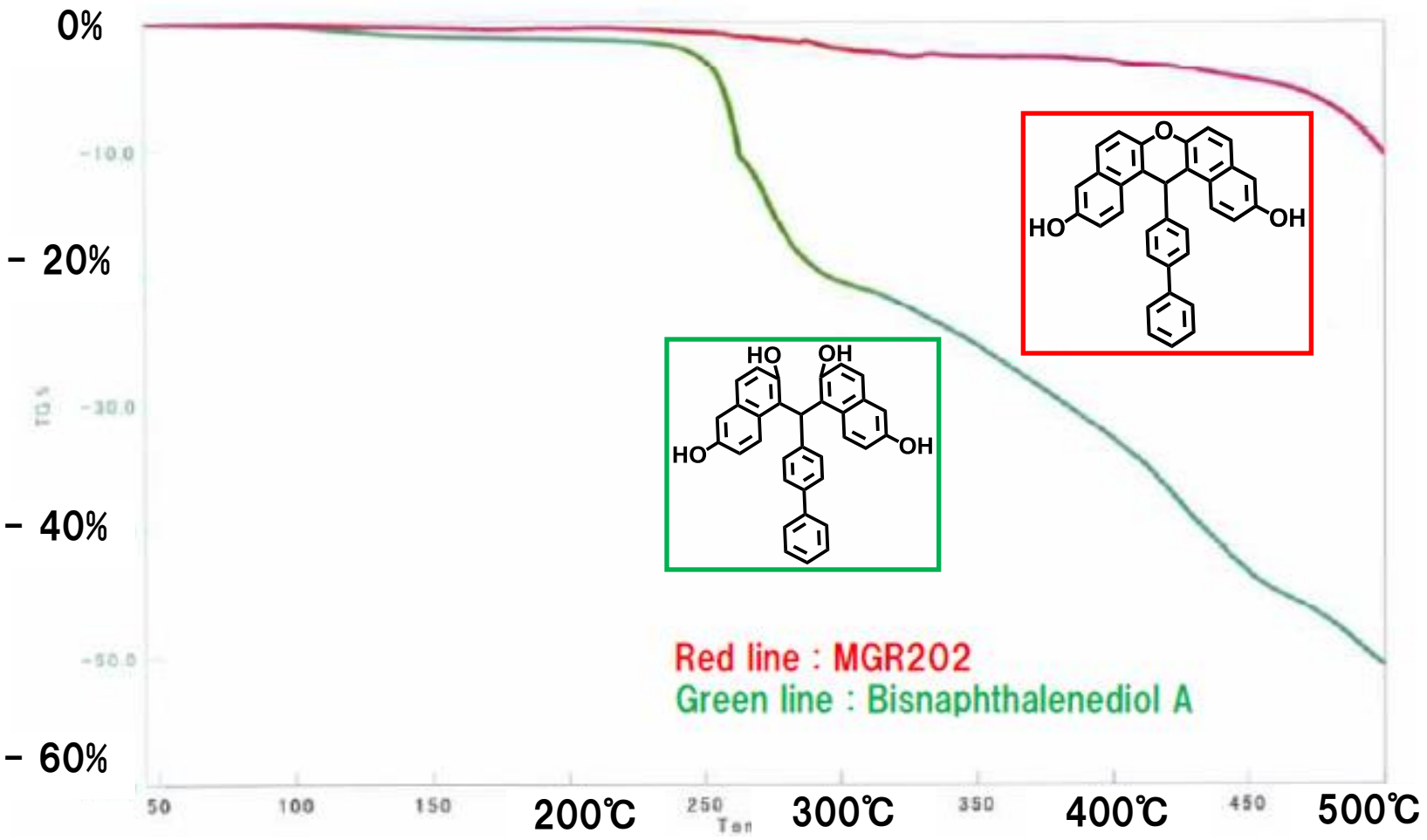
Solubility of MGR202 in resist solvents (A and alkaline developer (B

Sample	PGMEA	PGME	CHN	0.26N TMAHaq
MGR202	Soluble	Soluble	Soluble	Soluble

A = Insoluble: < 2 wt%; Barely soluble: 2-5 wt%; Soluble: > 5wt%,
B = Insoluble: < 5 nm/min; Barely soluble: 5-50 nm/min; Soluble: > 50nm/min

The solubility of MGR202 is good for the raw material for the molecular resist

Comparison between TGA themogram of MGR202 and that of Bisnaphthalenediol A

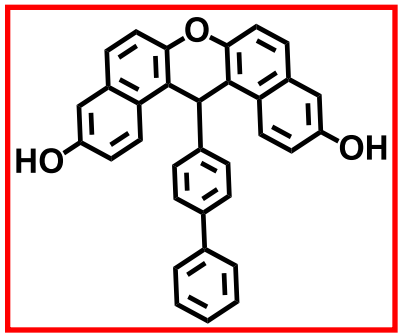


The xanthene structure was rigid structure and seem to increase the thermal stability.

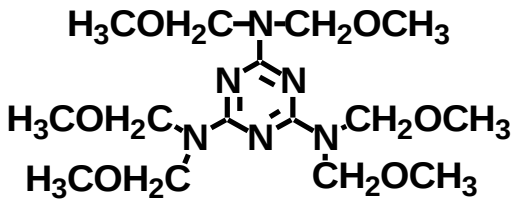
Experiment (Resist composition)

Matrix	: MGR202
PAG-1	: Sulfonium sulfonate
HMMM	: Hexamethoxymethylmelamine
Q-1	: Amine
PGME	: Propylene glycol monomethyl ether

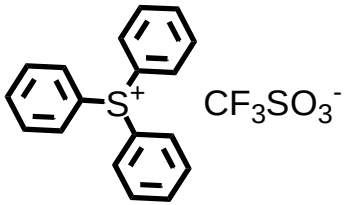
Difference of Resist A and Resist B :
1. Combination ratio of each ingredient, 2. PAB condition



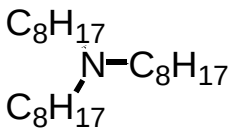
MGR202



HMMM



PAG-1



Q-1

Experiment (EB Patterning Evaluations)

Process Conditions:

Substrate: Organic layer (UL)
Film Thickness: 30−40nm
PAB: 110 - 120℃/90s
PEB: 110℃/90s
Dev.: TMAH 0.26N 60s

EB Patterning Evaluations:

- Apparatus
  Ultra−High Precision EBL System at MGC
  (ELS−7500 : Acceleration Voltage 50 keV)
  at Mitsubishi Gas Chemical (MGC)
- Analysis Conditions : SEM:S4800

EUVL Patterning Evaluations:

- Apparatus
  BL9B beamline at NewSUBARU
  synchrotron light source
  10.8m long undulator
  at Center for EUVL, University of Hyogo

ELS-7500

Etching Resistance

Process Conditions:

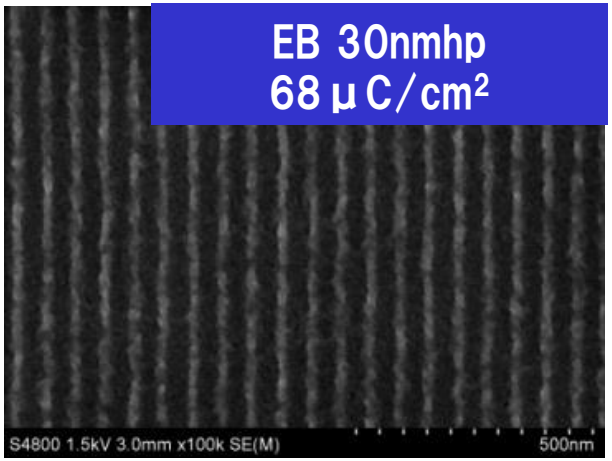
Reference: Novolac Resin
Bake Temperature: 110℃ (Novolac), 400℃ (MGR202)
Etching: 4Pa, 50W, O_2/CF_4=15/5cc

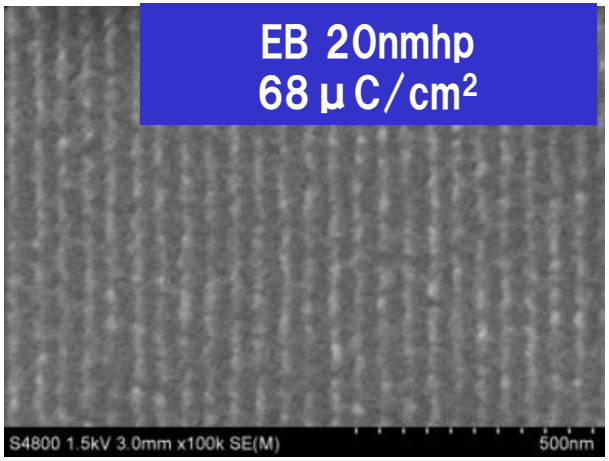
Etching Resistance Evaluations:

- Apparatus
  SAMCO Etching System (RIE-10NR)
  at Mitsubishi Gas Chemical (MGC)

RIE-10NR

EB Evaluation Data / SEM image (previous study)



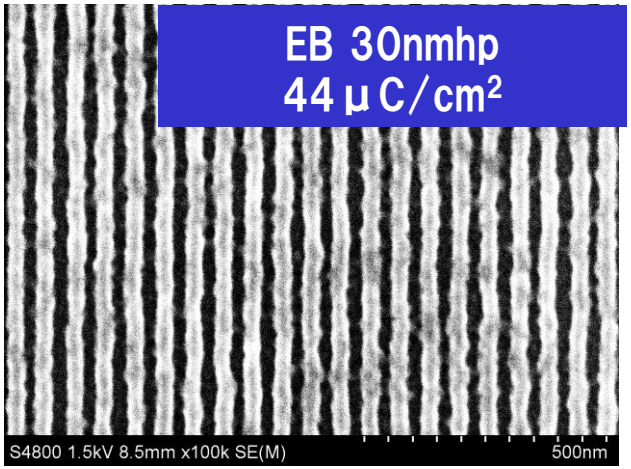


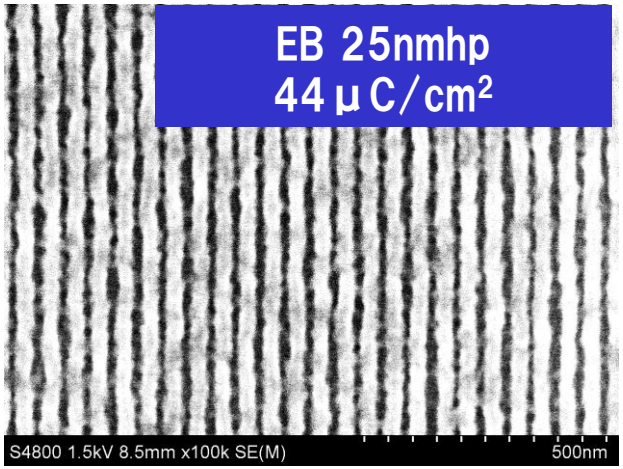
15nmhp
Not Resolve

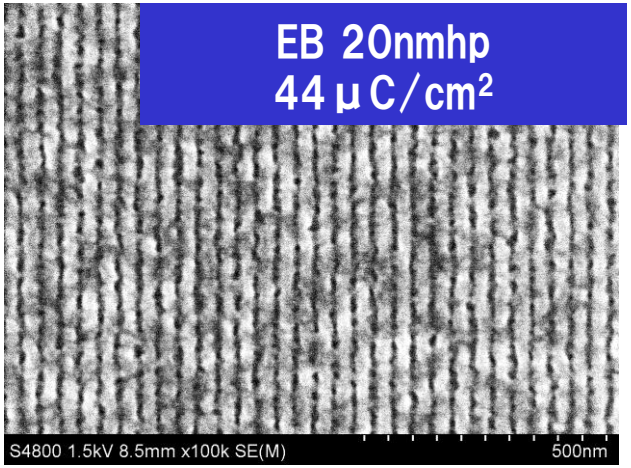
SEM images of Resist A based on MGR202 were resolved sub 30 nmhp patterns in 40nm thick films.

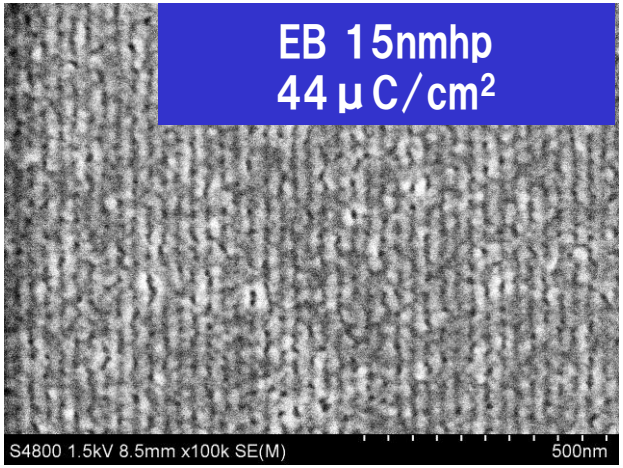
We optimized formulation and conditions.
And we built up Resist B.

EB Evaluation Data / SEM image



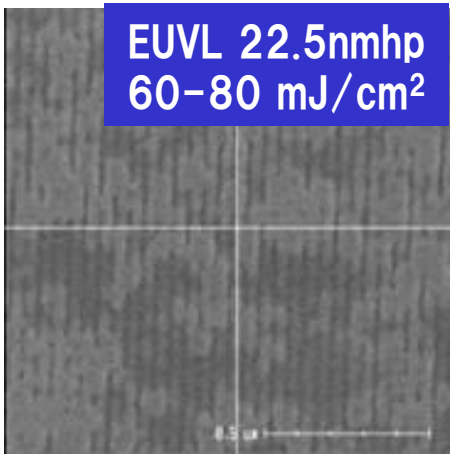


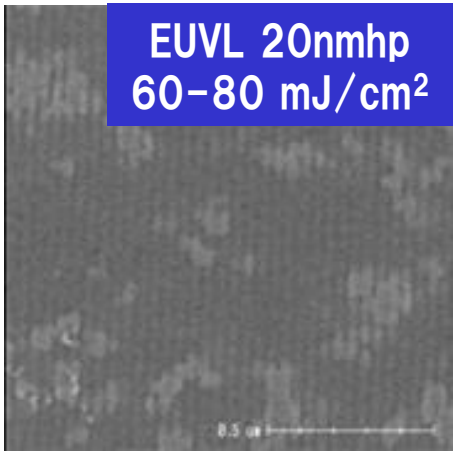




SEM images of Resist B based on MGR202 were resolved sub 20 nmhp patterns in 40nm thick films.

EUVL Evaluation Data / SEM image

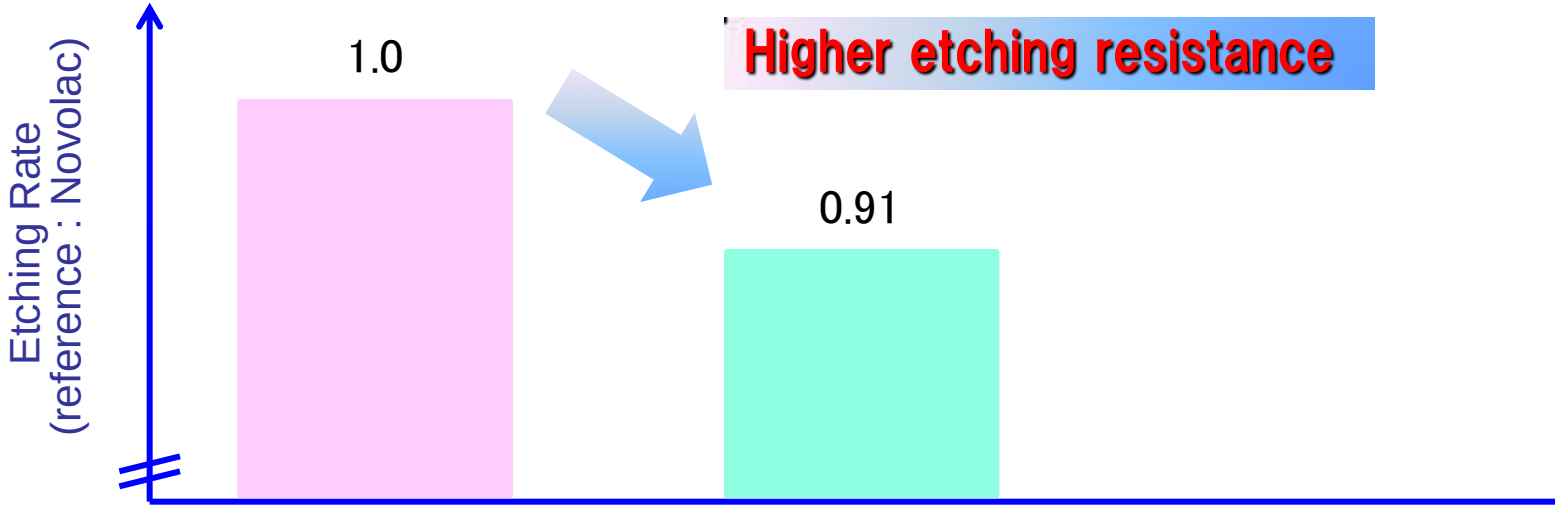


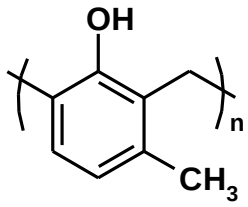


By courtesy of Center for EUVL, University of Hyogo

SEM images of Resist B based on MGR202 were resolved sub 22.5nmhp patterns in 32nm thick films.

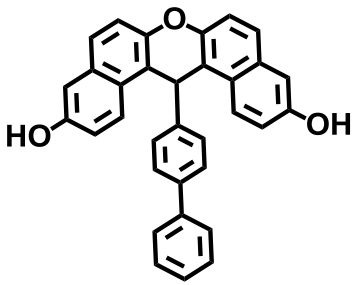
Etching Resistance





[Reference]

Novolac
(110℃ bake)



MGR202 (=NF0197)
(400℃ bake)

An etching rate of MGR202 is better than novolac rasin's.
It is expected that MGC's materials have good resolution, because we can use them coating thinly.

Summary

- We reported EB/EUVL patterning of the resist containing xanthendiol derivatives (13-biphenyl-13H-benzoxanthen-3,10-diol).

- The EB patterning result showed the resist containing xanthendiol derivative could resolve the 20 nm half-pitch pattern. Furthermore 15 nm half-pitch patterns were partially resolved.

- The EUVL patterning result also showed 20 nm half-pitch pattern.

- An etching rate is 0.91 times of the novolac resin.

- Future study is underway to improve etching-resistant of the resist by using xanthendiol derivatives.

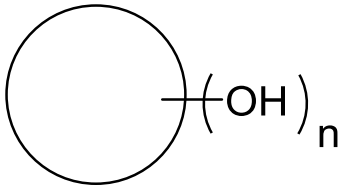
Acknowledgement

Prof. Takeo Watanabe of Center for EUVL, University of Hyogo gave great cooperation to us in EUV evaluation.
We express big gratitude.

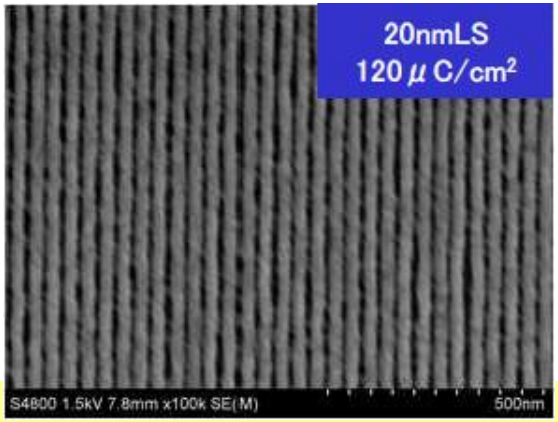
Future materials

We are developing the new xanthene derivative.

- shows high resolution.
- shows good etching resistance.

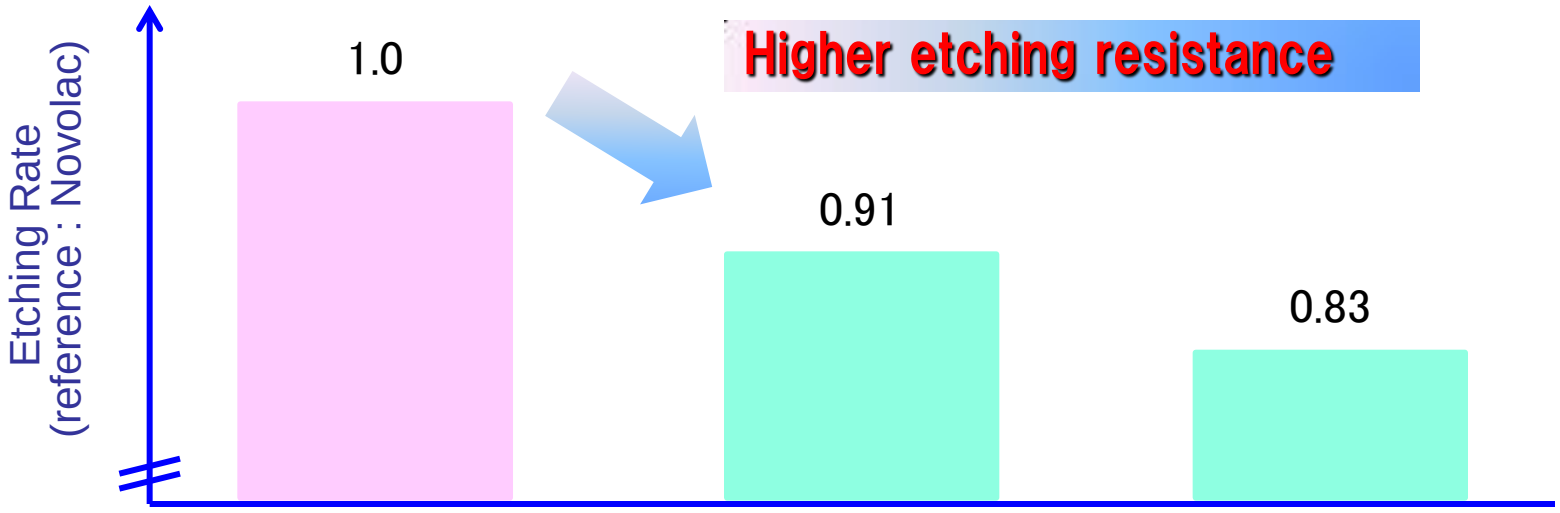


New xanthene derivative A



EB Evaluation Data
SEM image of the resist based on the new xanthene derivative could be resolved 20nmhp pattern in 40nm thick film.

Future materials



[Reference]

Novolac (110℃ bake)

MGR202 (=NF0197) (400℃ bake)

New Material B (400℃ bake)

The material, which has an etching rate better than MGR202, is available.